



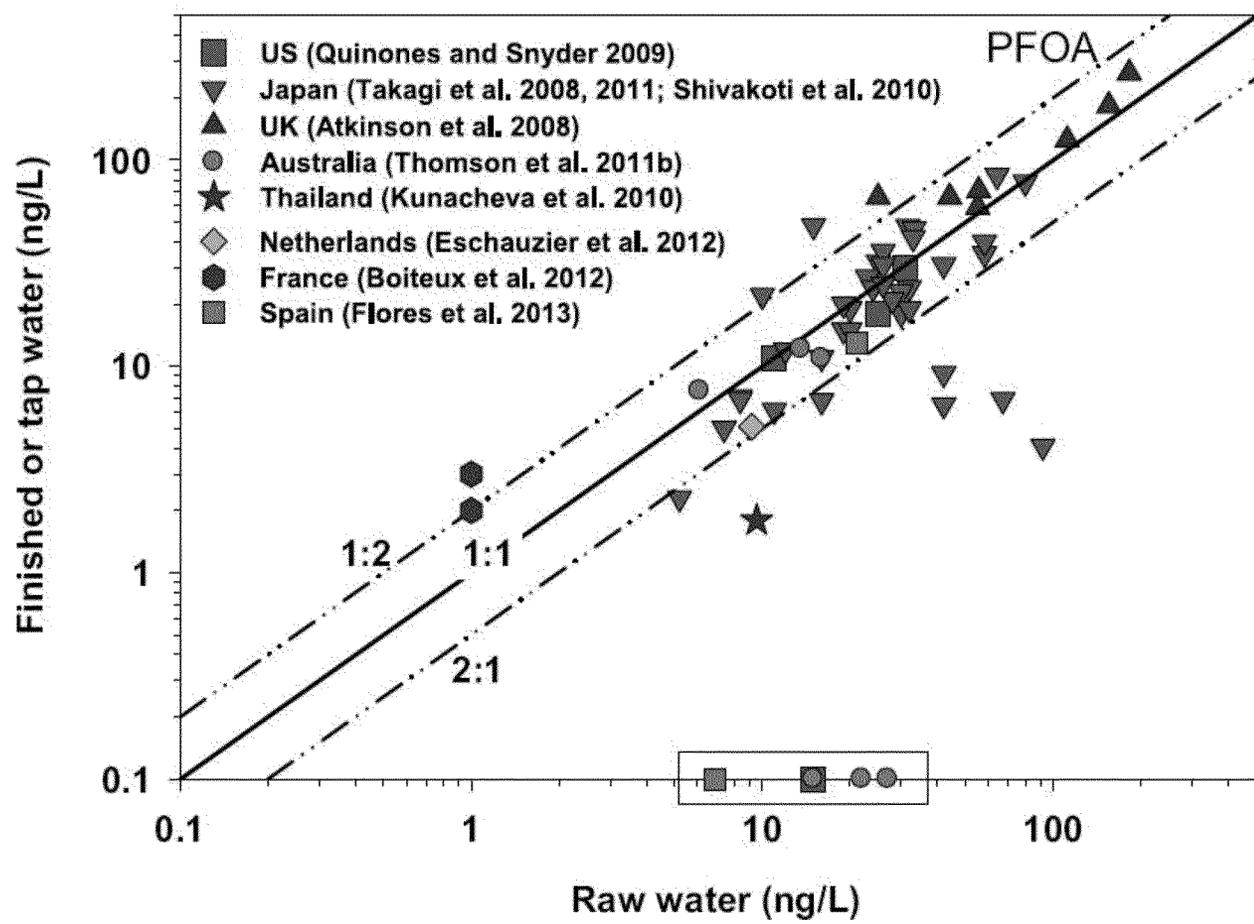
# Presentation Content

- Background
- Timeline
- Methods
- Nakayama et al., 2007 findings
- Strynar et al., 2015 findings
- Sun et al., 2016 findings
- Current efforts and findings

## Sources of PFAS Exposure for Humans

- Likely environmental sources include: industrial waste discharge at production and use facilities (fluoropolymer manufacturing, textile and carpet manufacture, metal/chrome plating), land application of contaminated bio-solids, use of aqueous film forming foam (AFFF) at military, airport and fire training facilities.
- Best documented source is contaminated drinking water near industrial production facilities or waste disposal e.g., Cottage Grove, Minnesota; Parkersburg, West Virginia; Dalton, Georgia; Decatur, Alabama; Arnsberg, Germany; Osaka, Japan *Lindstrom et al. 2011, Environ. Sci. & Technol. (45) 8015 – 8021*
- Food is also implicated in many studies, especially fish from contaminated waters, items contaminated by food packaging, and breast milk *Fromme et al. 2009, Inter. J. Hyg. & Envir. Heath (212) 239-270; Mogensen et al. 2015, Environ. Sci. & Technol. (49) 10466 - 10473*
- Workplace exposures significant for some sectors: manufacturing or services making or directly using PFAS, apparel sales, waste treatment *Nilsson et al. 2013 Environ. Sci.: Processes Impacts, 15, 814-822*

## PFAS Generally Not Removed During Conventional Drinking Water Treatment



Similar for PFOS, PFHxA and PFHxS

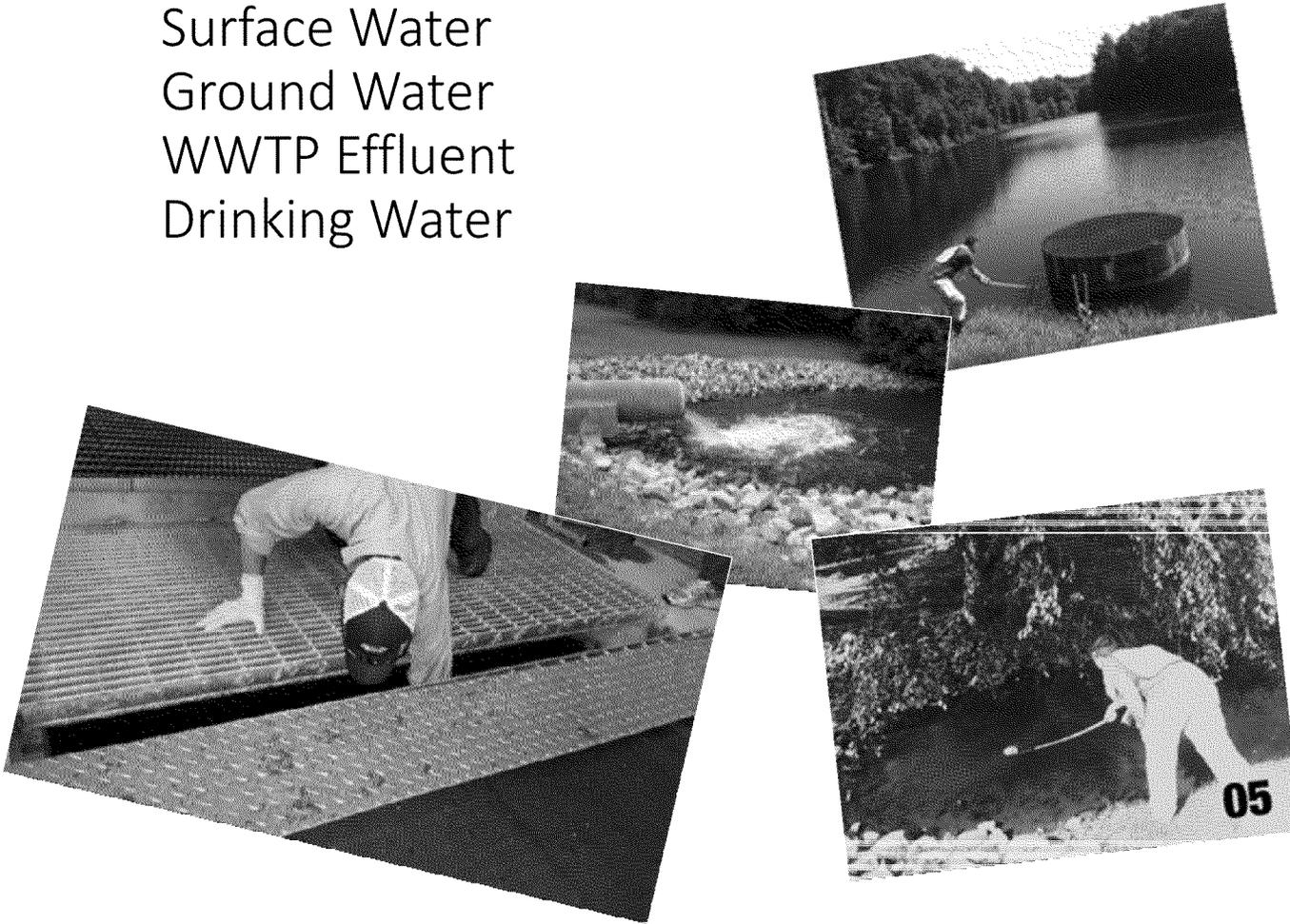
Rahman et al., (2014) *Water Research*, 50:318-340

# Timeline: US EPA/NERL Water PFAS Efforts

- 2007 Nakayama et al., PFAS in Cape Fear Watershed
- 2007-2008 Decatur, AL discovery of PFAS in bio-solids, soil, surface water, groundwater
- 2009 (January) Provisional Health Advisory (PHA) for PFOA and PFOS established 400 and 200 ng/L
- 2011-2012 Sampling of Cape Fear River for determination of replacement chemistries
- 2012 (November) Presentation at SETAC Long Beach CA – Identification of novel polyfluorinated compounds in natural waters using accurate mass TOFMS (GenX)
- 2013-2014 Collaborative study with NCSU with sampling of Cape Fear River and three municipalities (Pittsboro, Fayetteville, Wilmington, NC) for legacy and PFECA determination
- 2014 (November) Presentation at SETAC Vancouver, BC - Determination of perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in North Carolina surface water using high resolution mass spectrometry (GenX and eleven other novel chemicals)
- 2015 (August) Publication of Strynar et al., *“Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)”* ES&T
- 2016 (May) OW Health Advisory for PFOS and PFOA set at 70 ng/L
- 2016 (November) Publication of Sun et al., *“Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina”* ES&T Letters
- 2017 (June) Reporting of PFECAs in CFR and Wilmington drinking water – Star News Online

# NERL/EMMD Water Analysis Method

Surface Water  
Ground Water  
WWTP Effluent  
Drinking Water



# Some Typical PFAS



Perfluorocarboxylic acids  
(ex. PFOA)



Perfluorosulfonic acids  
(ex. PFOS)



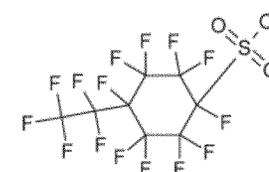
Fluorotelomer alcohol  
(ex. 8:2 FTOH)



Perfluorophosphonic/phosphinic acids  
(ex. If R=OH then PFOPA  
If R=C8 perfluoroalkane then 8:8 PFPi)



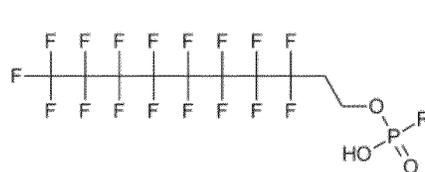
Perfluorosulfonamide  
(ex. FOSA)



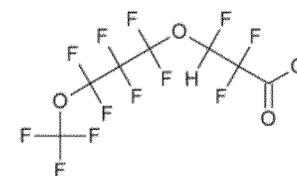
Perfluorinated cyclo sulfonates  
(ex. PFECHS)



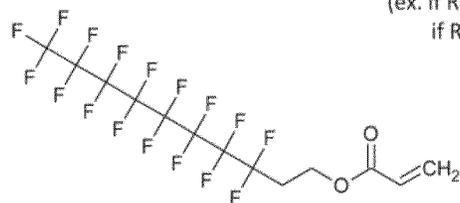
Perfluorosulfonamidoethanol  
(ex. N-EtFOSE)



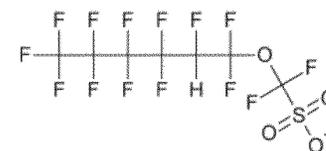
Fluorotelomer phosphate esters  
(ex. if R= OH then 8:2 monoPAP  
if R= 8:2 FTO ester then 8:2 diPAP)



Polyfluorinated ether carboxylates  
(ex. 4,8-dioxa-3H-perfluorononanoate)



Polyfluorinated polymeric unit  
(ex. 1H,1H,2H,2H-perfluorodecyl acrylate)



Polyfluorinated ether sulfonates  
(ex. Perfluoro [hexyl ethyl ether sulfonate])

**Analytes (n=24 native; n=19 isotope labeled)**

Wellington PFAC-24PAR (2 ng/uL) \$250/1.2 mL

	Analyte Name	Acronym	CAS Number
N-1	Perfluorotetradecanoic acid	PFTreA	376-06-7
N-2	Perfluorotridecanoic acid	PFTriA	72629-94-8
N-3	Perfluorododecanoic acid	PFDoA	307-55-1
N-4	Perfluoroundecanoic acid	PFUnA	2058-94-8
N-5	Perfluorodecanoic acid	PFDA	335-76-2
N-6	Perfluorononanoic acid	PFNA	375-95-1
N-7	Perfluorooctanoic acid	PFOA	335-67-1
N-8	Perfluoroheptanoic acid	PFHpA	375-85-9
N-9	Perfluorohexanoic acid	PFHxA	307-24-4
N-10	Perfluoropentanoic acid	PFPeA	2706-90-3
N-11	Perfluorobutanoic acid	PFBA	375-22-4
N-12	Perfluorodecanesulfonate	PFDS	335-77-3
N-13	Perfluorononanesulfonate	PFNS	68259-12-1
N-14	Perfluorooctanesulfonate	PFOS	1763-23-1
N-15	Perfluoroheptanesulfonate	PFHpS	375-92-8
N-16	Perfluorohexanesulfonate	PFHxS	355-46-4
N-17	Perfluoropentanesulfonate	PFPeS	2706-91-4
N-18	Perfluorobutanesulfonate	PFBS	375-73-5
N-19	Perfluorooctanesulfonamide	PFOSA	754-91-6
N-20	Fluorotelomer sulfonate 8:2	FtS 8:2	39108-34-4
N-21	Fluorotelomer sulfonate 6:2	FtS 6:2	27619-97-2
N-22	Fluorotelomer sulfonate 4:2	FtS 4:2	NA
N-23	N-ethyl-N-((heptadecafluorooctyl)sulfonyl)glycine	NEtFOSAA	2991-50-6
N-24	N-(Heptadecafluorooctylsulfonyl)-N-methylglycine	NMeFOSAA	2355-31-9

## Analytes (n=24 native; n=19 isotope labeled)

Wellington MPFAC-24ES (1 ng/uL) \$700/1.2 mL

	Analyte Name	Acronym
	PERFLUOROALKYLCARBOXYLATES (PFCAs)	
L-1	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]tetradecanoic acid	M2PFTeDA
L-2	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]dodecanoic acid	MPFDoA
L-3	Perfluoro-n-[1,2,3,4,5,6,7- <sup>13</sup> C <sub>7</sub> ]undecanoic acid	M7PFUdA
L-4	Perfluoro-n-[1,2,3,4,5,6- <sup>13</sup> C <sub>6</sub> ]decanoic acid	M6PFDA
L-5	Perfluoro-n-[ <sup>13</sup> C <sub>9</sub> ]nonanoic acid	M9PFNA
L-6	Perfluoro-n-[ <sup>13</sup> C <sub>8</sub> ]octanoic acid	M8PFOA
L-7	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]heptanoic acid	M4PFHpA
L-8	Perfluoro-n-[1,2,3,4,6- <sup>13</sup> C <sub>5</sub> ]hexanoic acid	M5PFHxA
L-9	Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]pentanoic acid	M5PFPeA
L-10	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid	MPFBA
	PERFLUOROALKYLSULFONATES (PFASs)	
L-11	Sodium perfluoro-[ <sup>13</sup> C <sub>8</sub> ]octanesulfonate	M8PFOS
L-12	Sodium perfluoro-1-[1,2,3- <sup>13</sup> C <sub>3</sub> ]hexanesulfonate	M3PFHxS
L-13	Sodium perfluoro-1-[2,3,4- <sup>13</sup> C <sub>3</sub> ]butanesulfonate	M3PFBS
	PERFLUOROCTANESULFONAMIDES (FOSAs)	
L-14	Perfluoro-1-[ <sup>13</sup> C <sub>8</sub> ]octanesulfonamide	M8FOSA-I
	TELOMER SULFONATES	
L-15	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]decane sulfonate (8:2)	M2-8:2FTS
L-16	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]octane sulfonate (6:2)	M2-6:2FTS
L-17	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]hexane sulfonate (4:2)	M2-4:2FTS
	PERFLUOROCTANESULFONAMIDOACETIC ACIDS	
L-18	N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid	d5-N-EtFOSAA
L-19	N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid	d3-N-MeFOSAA

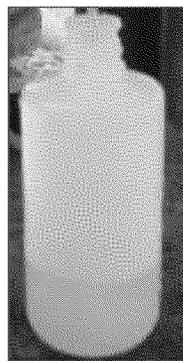
# Quality Assurance – Quality Control

- Trip spike(s) (ex. 50 ng/L) MOST PEOPLE DO NOT DO THIS
- Trip blank (DI)
- Replication (>10%)
- Occasionally standard addition
- Extracted calibration curves

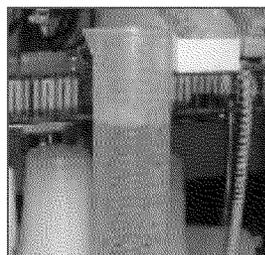


# Method Summary – Sample Processing

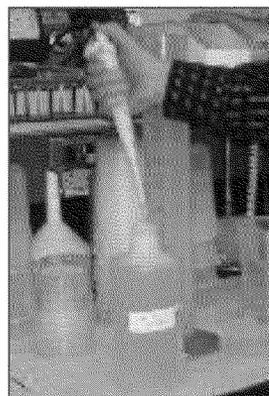
Nakayama et al., 2009



1 L HDPE bottles  
5 mL 1:1 HNO<sub>3</sub> (35%):DI  
Shipped ambient



Pour water out  
of sample bottle  
for volume  
measurement



Wash bottle with 10 mL  
MeOH, add water back  
to bottle, add IS Shake



Filter entire contents  
Whatman GF/A 1.7 um

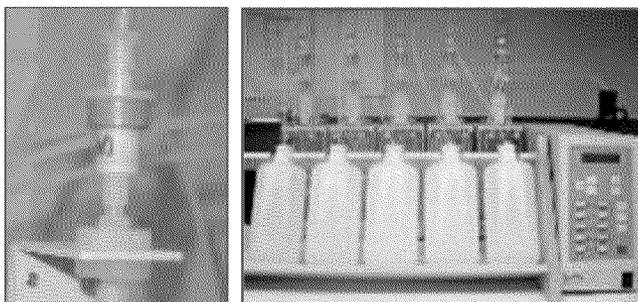
All samples  
Treated same  
way

- Trip Spike
- Blanks
- Unknowns
- Calibration



Add filtered water back into original  
bottle

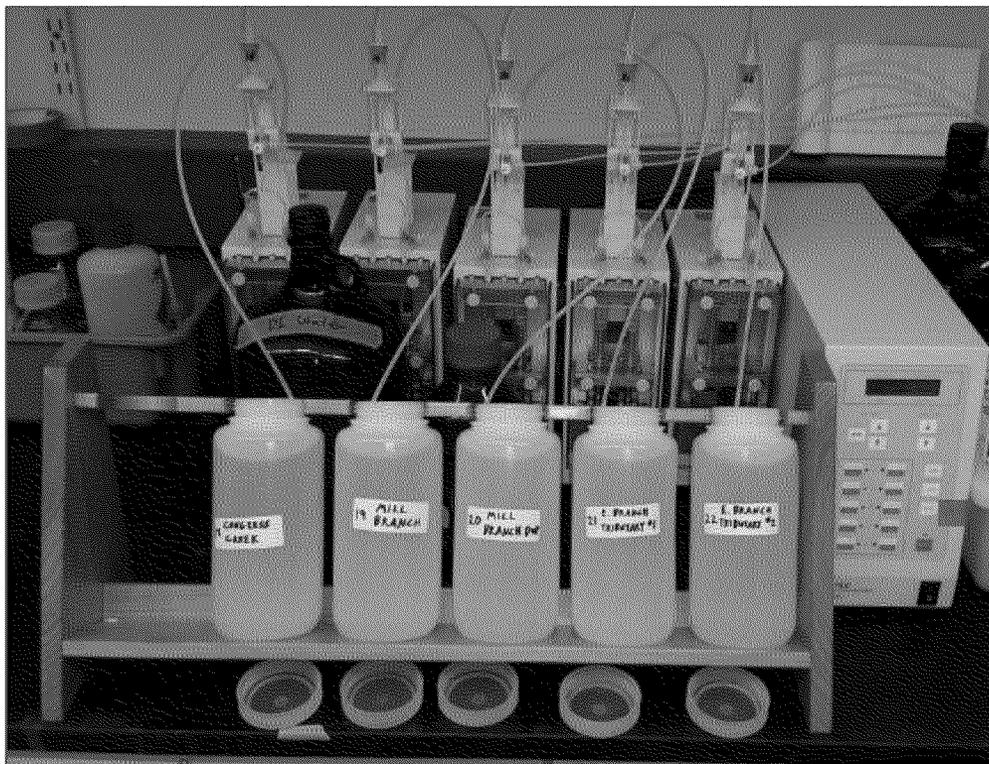
Subsample 500 mL  
Store 500 mL



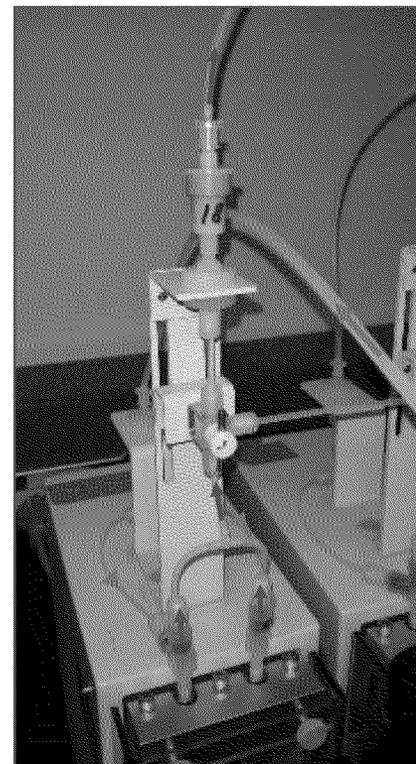
Load onto SPE tube  
Waters Plus style WAX

Elute for  
LC/MS-MS  
analysis

# Positive Displacement Sample Concentration



CHRATEC Sep-Pak Concentrator  
SPC 10-C (10 ml/min)



Waters Oasis WAX-plus

# Sample Elution



Note: Rack modified to fit 15 mL BD Falcon tubes

Wash:  
4 mL pH 4.0 buffer  
(Acetate/Acetic Acid water)

4 mL methanol

Elute:  
4 mL NH<sub>4</sub>OH/MeOH

Evaporate:  
~15-20 minutes 40°C N<sub>2</sub>  
TurboVap concentrator

~ 0.5 – 1.0 mL

Sample prep for analysis:  
Prepare sample to match  
starting conditions of UPLC  
gradient (75:25 aqu:MeOH)

# Samples That Exceed Calibration Curve

Estimate concentration based on exceedance analysis

Dilute sample (analyte and IS presence) with DI lab water (IS added)  
(ex 1:1, 2:1, 5:1 10:1) aiming for midpoint of calibration curve.

Example: Standard curve 10 – 1000 ng/L PFOA  
Sample estimated to be 1600 ng/L

Dilute sample into new HDPE bottle:

1 part (250 mL prepared water sample with IS spike and analytes)

1 part(250 mL) DI water with IS spike at same level as real sample

Re-extract, elute and analyze.

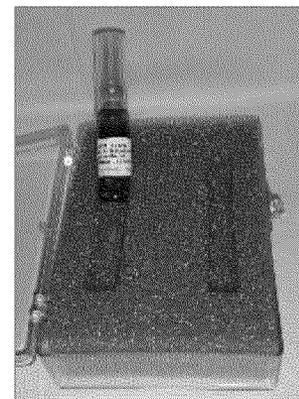
Calibrate against existing calibration curve.

# Source of Analytical Standards

Stable Isotope Labeled ( $^{13}\text{C}$ ,  $^{18}\text{O}$ , D):

Wellington Labs

Cambridge Isotopes Labs



Native:

Wellington Labs (Mixtures – 1-2 ng/uL; Individual 50 ng/uL)

Sigma-Aldrich

Synquest Labs

Oakwood Products

Manufacturer (industrial mixtures 3M, DuPont,  
Mason Chemicals)



## Method Summary – Water Sample Collection

SS Kemmerer sampler



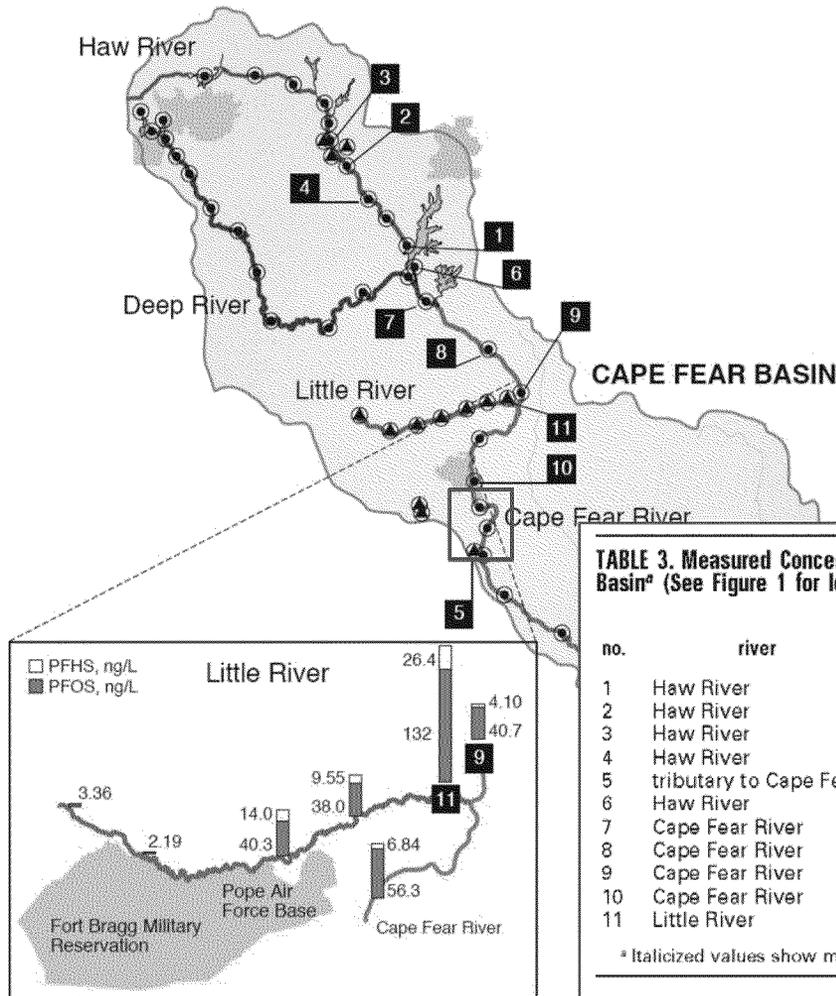
Lab-made dip sampler



Nalgene 1L HDPE bottles: PFAS free; Prefer wide mouth bottles

# Water Sampling Cape Fear River, NC

Nakayama et al., 2007



**TABLE 3. Measured Concentrations at the Eleven Sites with the Highest Total Concentrations of PFCs in the Cape Fear River Basin<sup>a</sup> (See Figure 1 for locations)**

no.	river	C12 (ng/L)	C11 (ng/L)	C10 (ng/L)	C9 (ng/L)	C8 (ng/L)	C7 (ng/L)	C6 (ng/L)	PFOS (ng/L)	PFHS (ng/L)	PFBS (ng/L)	total (ng/L)
1	Haw River	<i>4.46</i>	<b>52.1</b>	<b>120</b>	<b>194</b>	<b>287</b>	118	21.7	127	8.43	<b>9.41</b>	942
2	Haw River	3.20	28.7	112	157	200	66.8	14.5	33.4	7.87	2.61	626
3	Haw River	3.29	27.6	109	157	191	59.2	13.7	36.4	9.49	3.04	609
4	Haw River	1.98	20.0	88.2	151	201	58.2	13.2	31.5	7.49	2.88	574
5	tributary to Cape Fear	2.26	15.0	19.6	71.2	58.6	<b>329</b>	<b>23.0</b>	30.0	3.36	ND	531
6	Haw River	1.18	8.87	31.0	72.1	152	58.3	13.5	31.2	7.70	ND	376
7	Cape Fear River	< LOQ	3.34	13.2	34.8	70.3	24.0	7.84	66.7	5.59	ND	227
8	Cape Fear River	1.14	6.39	17.2	35.7	71.5	26.9	9.35	50.4	4.82	ND	223
9	Cape Fear River	1.23	6.75	17.1	38.0	72.7	23.7	7.05	40.7	4.10	ND	211
10	Cape Fear River	< LOQ	7.55	19.3	31.2	46.8	13.9	4.62	56.3	6.84	2.12	189
11	Little River	< LOQ	< LOQ	2.17	2.24	12.6	3.38	3.23	<b>132</b>	<b>26.4</b>	3.20	185

<sup>a</sup> Italicized values show maximal concentrations of each compound.



First Sampling 2011-2012

Presented at SETAC 2012

Follow-up sampling 2013-2013

Presented at SETAC 2014



Water Intake

Current Outfall

Former Outfall

The Chemours Company

Kuraray

US Lock & Dam

William O Huske

Cap Fear River

87

1303

1303

1303

Georgia Bayway

Map

Google

Imagery ©2017 DigitalGlobe, USDA Farm Service Agency, Map data ©2017 Google 3D Earth view is not available Terms Send feedback

# Legacy PFAS found in Cape Fear Water

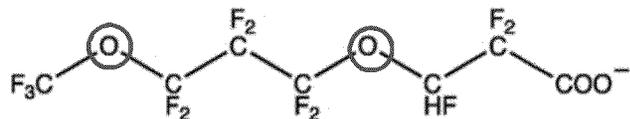


Analyte	001	002	003	004	005	006	007	008	008	009
C4	23	502	3761	6	4	0	8	7	5	3
C5	441	5607	43590*	17	9	1	32	46	12	9
PFBS	4	5	3	4	5	2	9	5	6	4
C6	17	90	434	18	12	2	27	16	18	14
C7	37	599	3873	14	17	0	11	20	21	9
PFHS	7	12	10	9	7	4	9	10	9	22
C8	32	39	71	33	25	2	38	36	41	18
C9	13	34	127	7	11	1	6	8	11	5
PFOS	19	27	26	17	23	0	0	16	18	14
C10	10	17	12	11	0	3	3	8	10	5

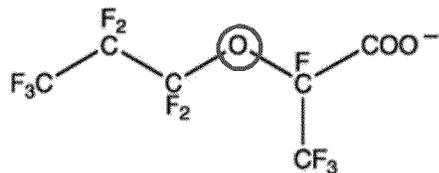
items in red exceed the standard curve high end of 500 ng/L; 10x diluted and re-analyzed; \* still exceed curve and are estimated

## Fluoropolymer manufacture

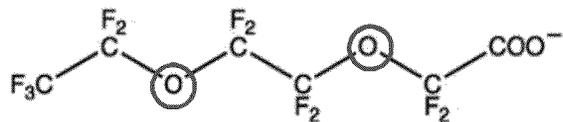
ADONA (CAS No. 958445-44-8)



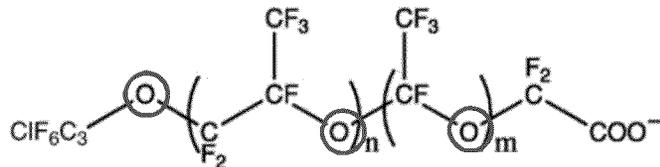
GenX (CAS No. 62037-80-3)



Asahi's product (CAS No. 908020-52-0)

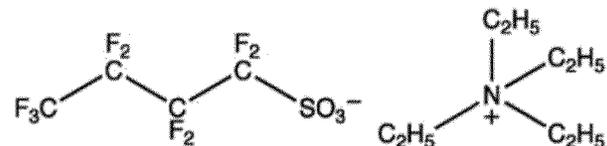


Solvay's product (CAS No. 329238-24-6)

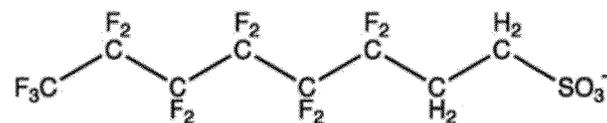


## Metal plating

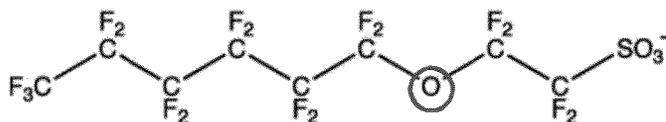
N(Et)<sub>4</sub>-PFBS (CAS No. 25628-08-4)



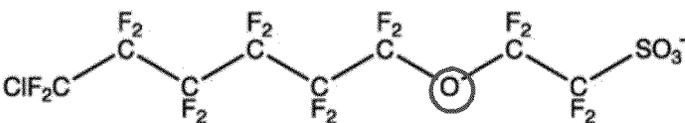
6:2 FTSA (CAS No. 27619-97-2)



F-53 (CAS No. 754925-54-7)



F-53B (CAS No. 73606-19-6)



Wang et al., 2013 Environment  
International 60 (2013) 242–248

## Negative Mass Defect: Per- and Poly- fluorinated Compounds

Formula	Mass	C	H	N	O	P	S	Cl	F
		12.000000	1.007825	14.003074	15.994915	30.973762	31.972071	34.968853	18.998403
C <sub>8</sub> H <sub>18</sub>	114.1408506	8	18						
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	144.1150298	8	16		2				
C <sub>8</sub> HO <sub>2</sub> F <sub>15</sub>	413.9737023	8	1		2				15
C <sub>8</sub> HO <sub>3</sub> F <sub>15</sub>	429.9686169	8	1		3				15
C <sub>8</sub> HO <sub>3</sub> SF <sub>17</sub>	499.937494	8	1		3		1		17

Octane	114.1408506
Octanoic acid	144.1150298
PFOA	413.9737023
Perfluoro-4-ether-octanoic acid	429.9686169
PFOS	499.937494

Mass fragments of per and poly fluorinated compounds conserve negative mass defect

## Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

Mark Strynar,<sup>\*,†</sup> Sonia Dagnino,<sup>†,‡</sup> Rebecca McMahan,<sup>†,‡</sup> Shuang Liang,<sup>†,‡</sup> Andrew Lindstrom,<sup>†</sup> Erik Andersen,<sup>†</sup> Larry McMillan,<sup>§</sup> Michael Thurman,<sup>||</sup> Imma Ferrer,<sup>||</sup> and Carol Ball<sup>‡</sup>

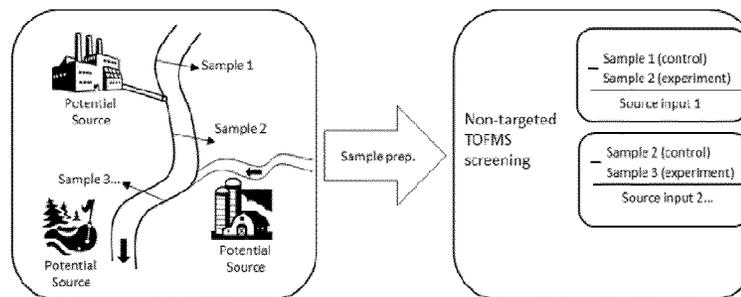
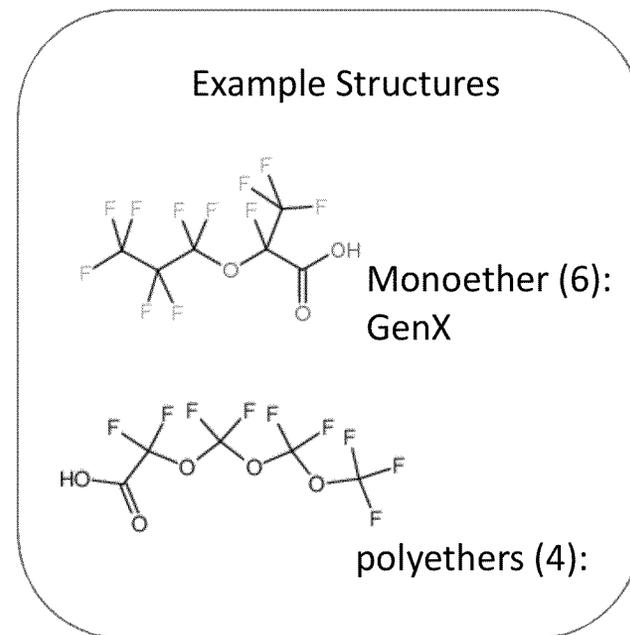


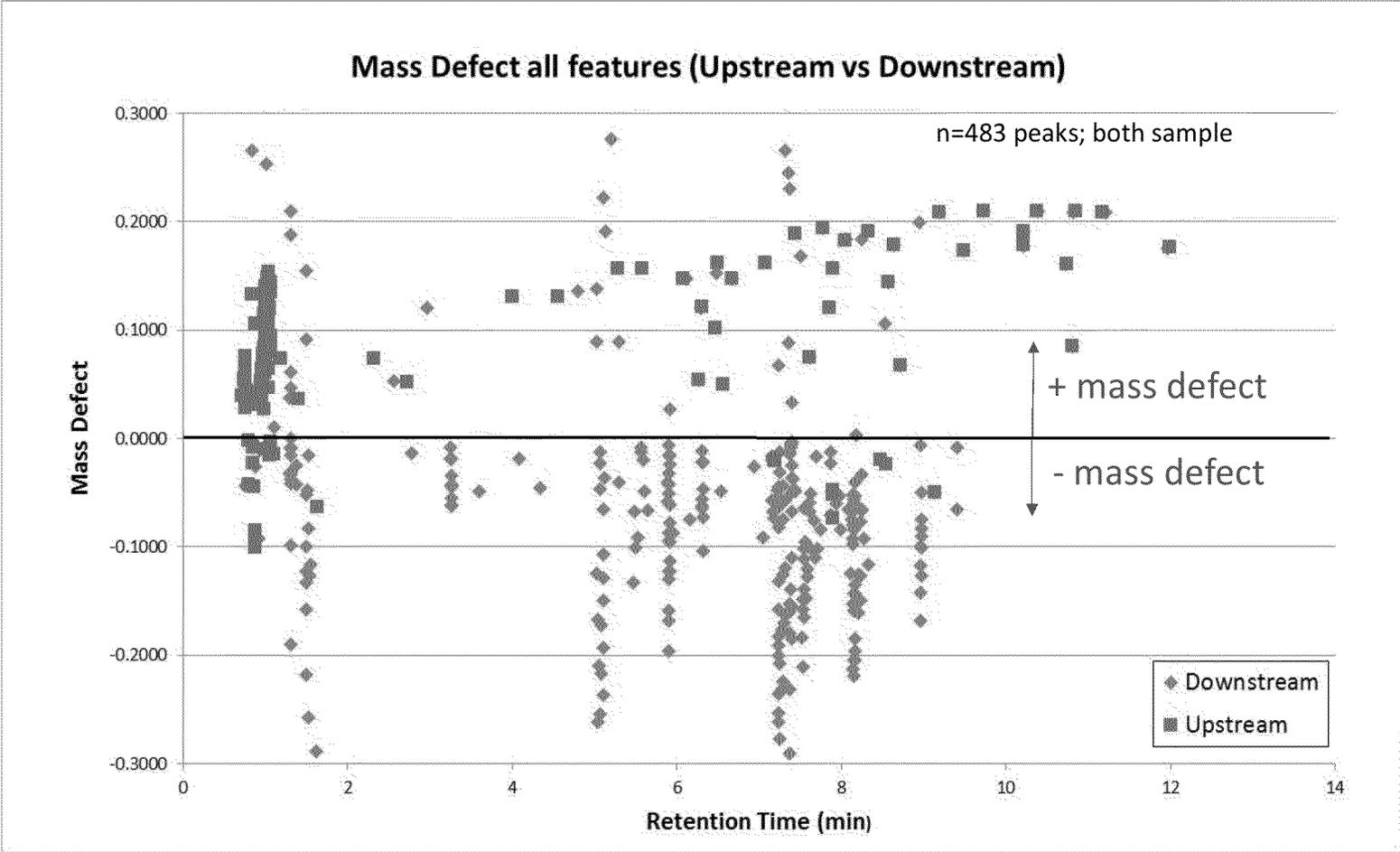
Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

number	formula	CAS no.	name	$[M]^+$	$[M - H]^-$ $m/z$	$[2M - 2H + Na]^-$ $m/z$	$[2M - H]^-$ $m/z$
<b>Monoether PFECAs</b>							
1	C <sub>3</sub> HF <sub>5</sub> O <sub>3</sub>			179.9846	178.9773	380.9438	358.9619
2	C <sub>4</sub> HF <sub>7</sub> O <sub>3</sub>			229.9813	228.9740	480.9372	458.9553
3	C <sub>5</sub> HF <sub>9</sub> O <sub>3</sub>	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	C <sub>6</sub> HF <sub>11</sub> O <sub>3</sub>	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427
5	C <sub>7</sub> HF <sub>13</sub> O <sub>3</sub>			379.9718	378.9645	780.9182	758.9363
6	C <sub>8</sub> HF <sub>15</sub> O <sub>3</sub>			429.9686	428.9613	880.9118	858.9299
<b>Polyether PFECAs</b>							
7	C <sub>7</sub> HF <sub>13</sub> O <sub>7</sub>	39492-91-6	perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	443.9515	442.9442	908.8776	886.8957
8	C <sub>6</sub> HF <sub>11</sub> O <sub>6</sub>	39492-90-5	perfluoro-3,5,7,9-butaoxadecanoic acid	377.9598	376.9525	776.8942	754.9123
9	C <sub>5</sub> HF <sub>9</sub> O <sub>5</sub>	39492-89-2	perfluoro-3,5,7-propaoxaoctanoic acid	311.9681	310.9608	644.9108	622.9289
10	C <sub>4</sub> HF <sub>7</sub> O <sub>4</sub>	39492-88-1	perfluoro-3,5-dioxahexanoic acid	245.9764	244.9691	512.9274	490.9455
<b>PFESAs</b>							
11	C <sub>7</sub> HF <sub>13</sub> O <sub>3</sub> S	66796-30-3 <sup>b</sup>		443.9337	442.9264		
12	C <sub>7</sub> H <sub>2</sub> F <sub>14</sub> O <sub>3</sub> S			463.9399	462.9326		

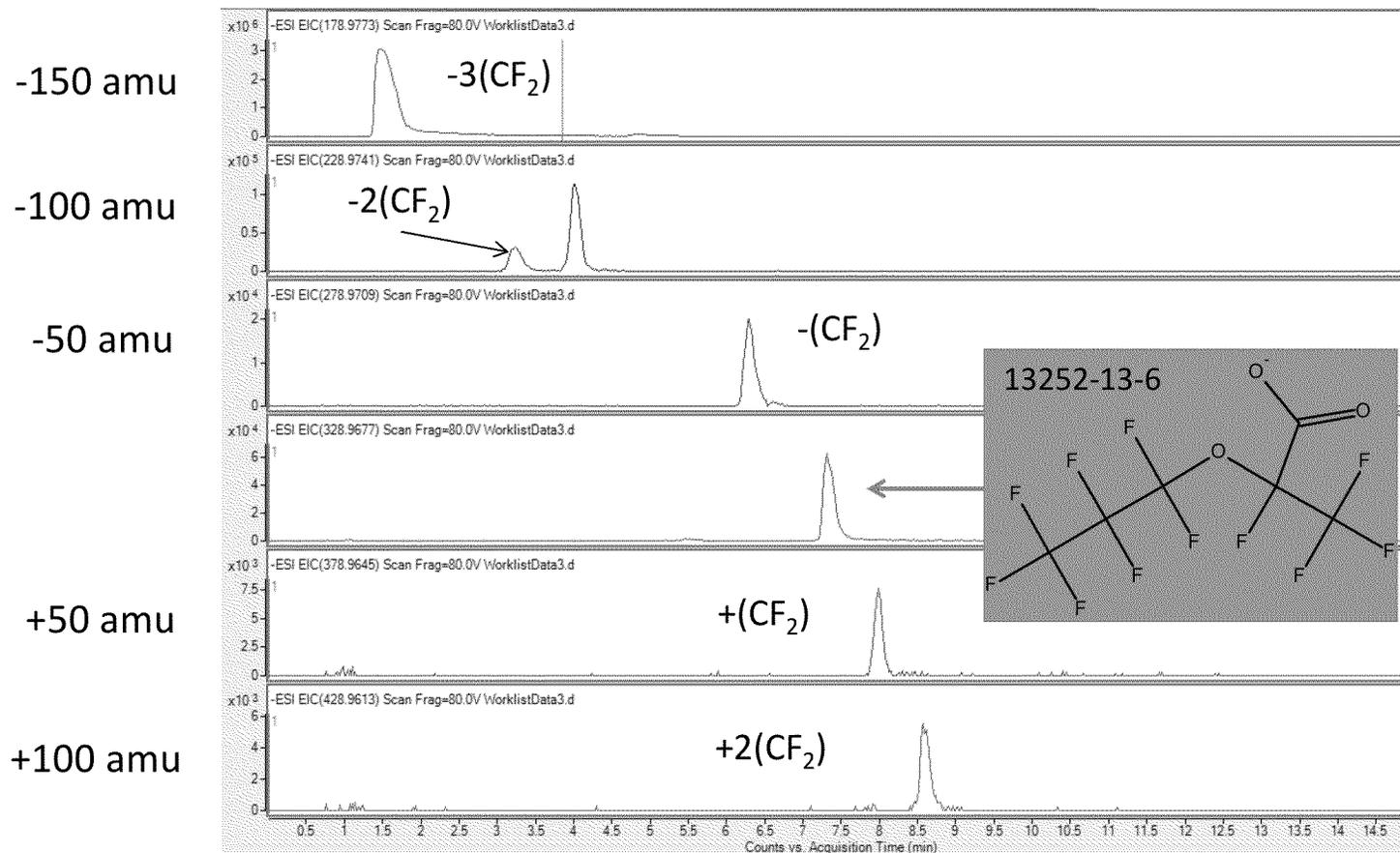


# Mass Defect Plot TOFMS data

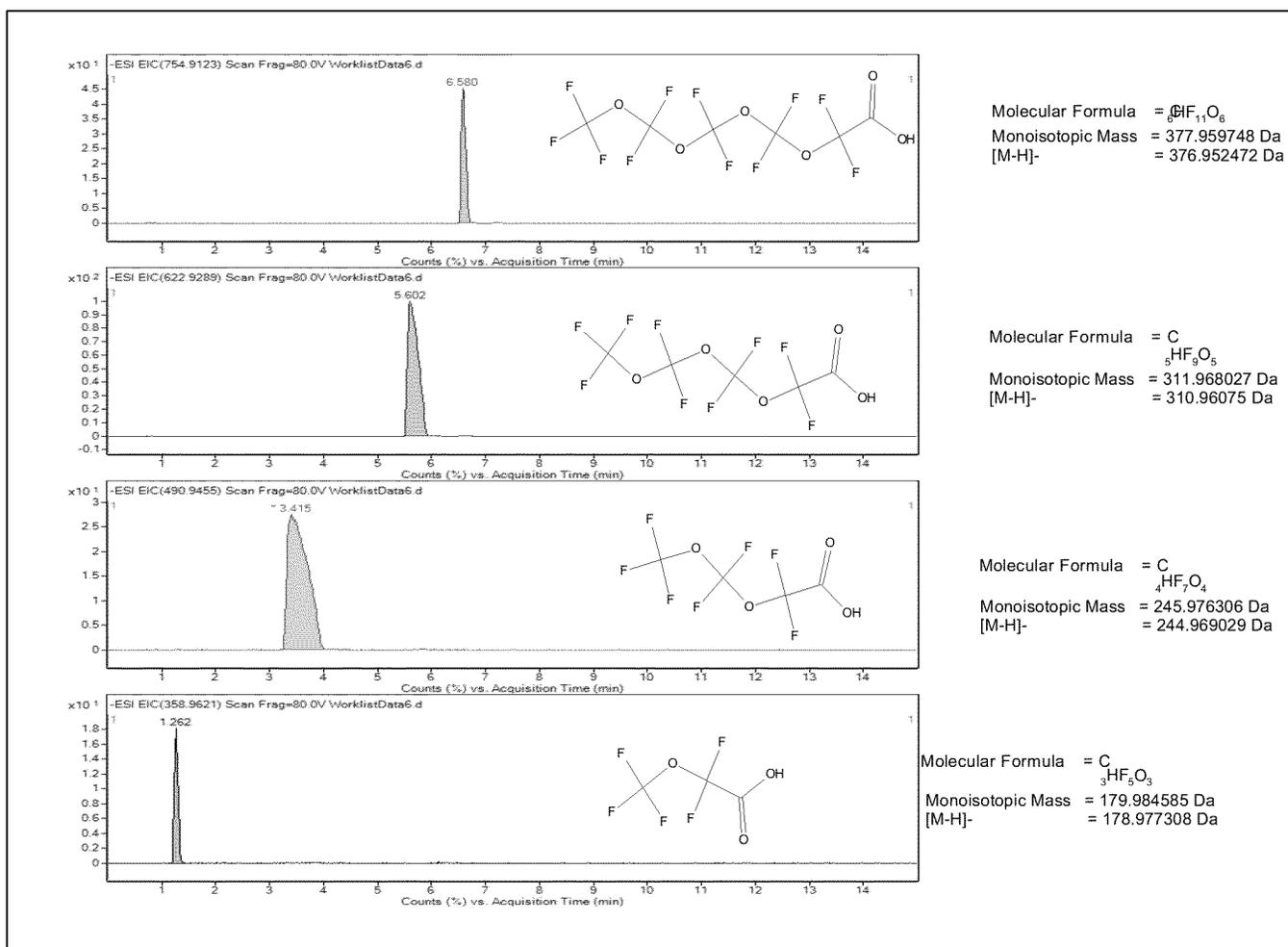
Accurate Mass – Nominal Mass = Mass Defect



# m/z Extracted Ion Chromatograph (EIC) Suspected polyfluorinated compound homologous series



# Homologous series NOT offset by CF<sub>2</sub> BUT CF<sub>2</sub>O



**Legacy and Emerging Perfluoroalkyl Substances Are Important  
Drinking Water Contaminants in the Cape Fear River Watershed of  
North Carolina**

Mei Sun,<sup>\*,†,‡,§</sup> Elisa Arevalo,<sup>‡</sup> Mark Strynar,<sup>§</sup> Andrew Lindstrom,<sup>§</sup> Michael Richardson,<sup>||</sup> Ben Kearns,<sup>||</sup>  
Adam Pickett,<sup>±</sup> Chris Smith,<sup>#</sup> and Detlef R. U. Knappe<sup>‡</sup>

June 7, 2017 story on in Wilmington Star Online News basis.

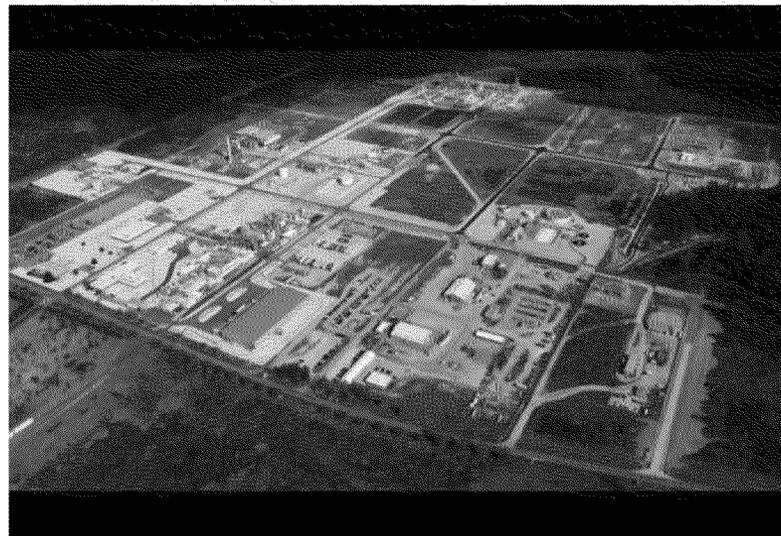
# Toxin taints CFPWA drinking water



### MOST POPULAR

- 1 Carolina Surf condos - in danger of collapse - condemned, evacuated  
Jul 2 at 5:50 AM
- 2 Man injured by hook, not bit by shark at Wrightsville Beach  
Jun 30 at 1:43 PM
- 3 Murder suspect had other charges pending  
Jul 2 at 5:44 AM
- 4 Residents not allowed back into Carolina Surf condos  
Jul 4 at 7:33 AM

### OUR PICKS



▲ HIDE CAPTION

A 2000 aerial photo of Fayetteville Works on the Cumberland-Bladen county line. The site, home to several plants, one of which makes GenX, is about 100 miles upstream from Wilmington. [COURTESY OF THE FAYETTEVILLE OBSERVER]

Cape Fear River  
Fayetteville to Wilmington, NC

By Vaughn Hagerly StarNews Correspondent

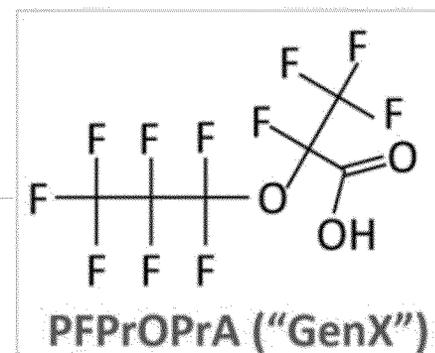
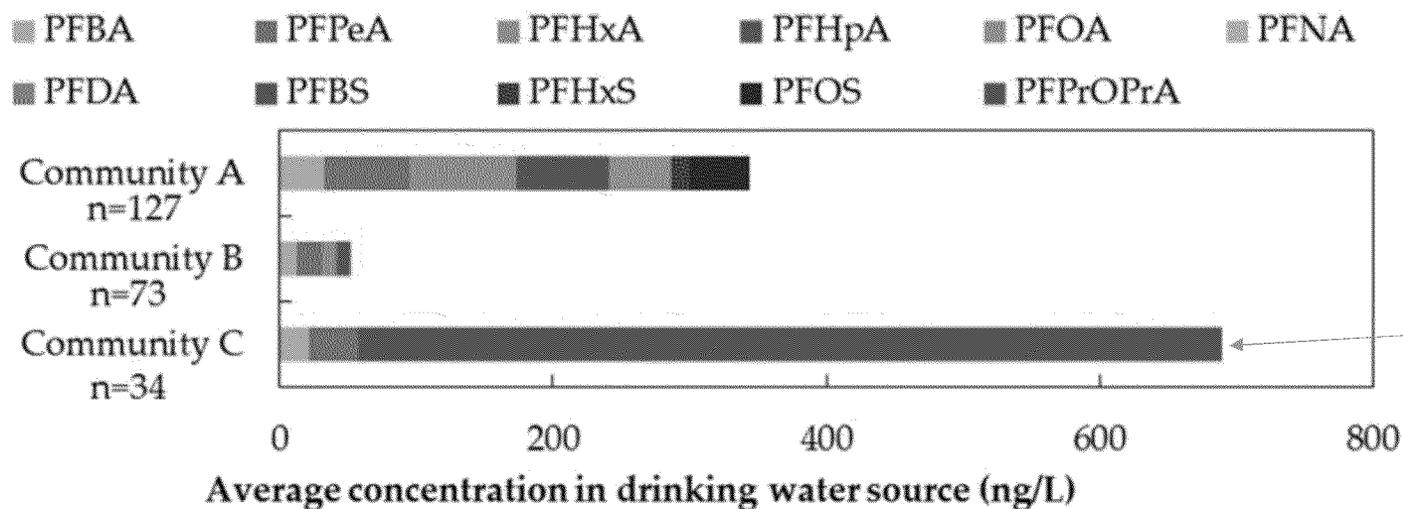
Posted Jun 7, 2017 at 10:31 AM

Updated Jun 8, 2017 at 10:38 AM

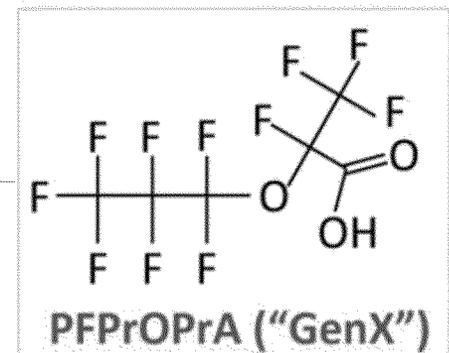
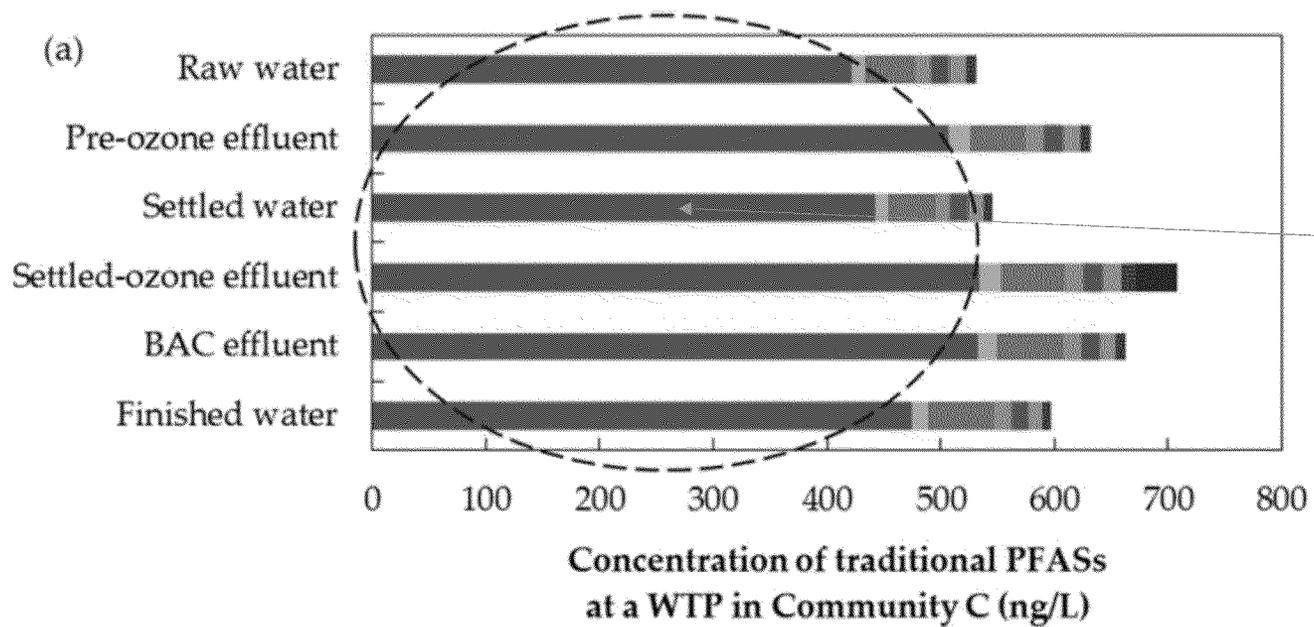


Utility can't filter out chemical produced upriver

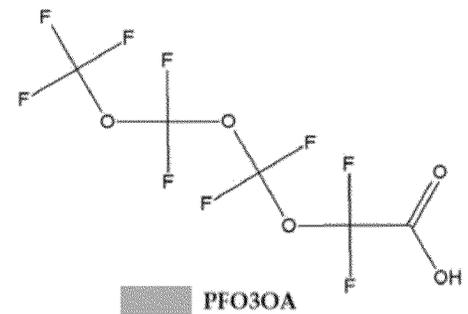
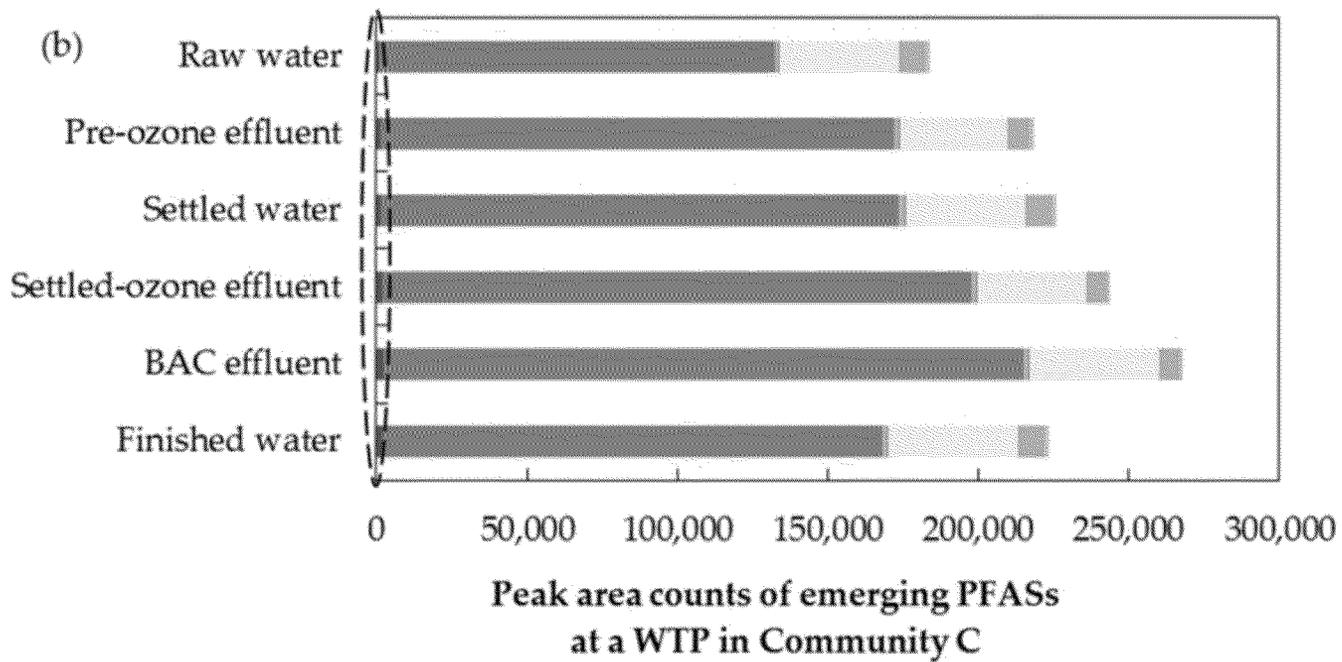




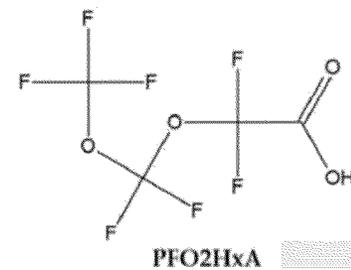
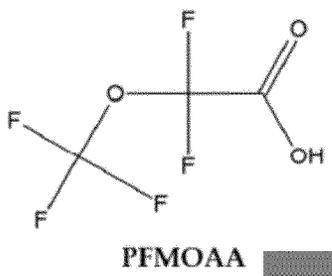
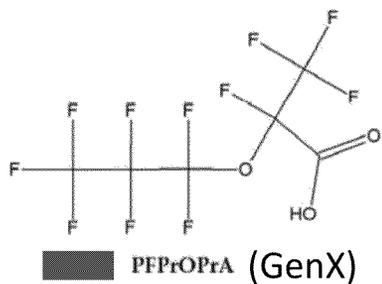
**Figure 1.** Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.



- PFPrOPrA   ■ PFBA   ■ PFPeA   ■ PFHxA   ■ PFHpA   ■ PFOA
- PFNA   ■ PFDA   ■ PFBS   ■ PFHS   ■ PFOS



■ PFPrOPrA      ■ PFMOAA      ■ PFMOPrA      ■ PFMOBA  
 ■ PFO2HxA      ■ PFO3OA      ■ PFO4DA

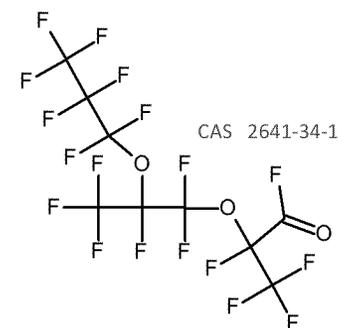
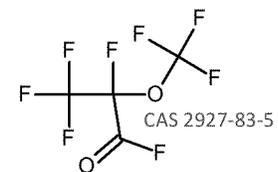
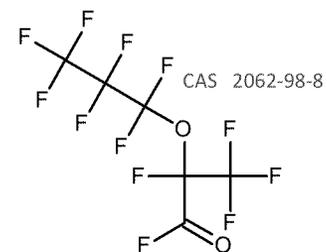
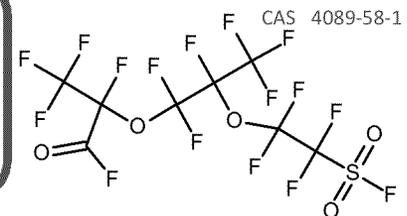
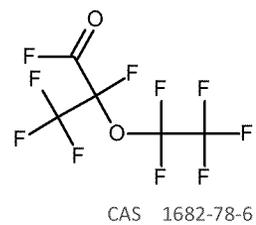
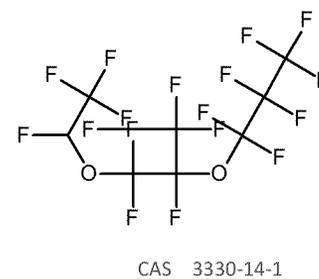
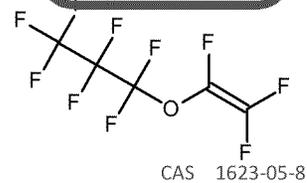
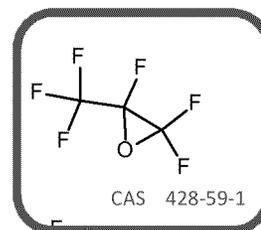
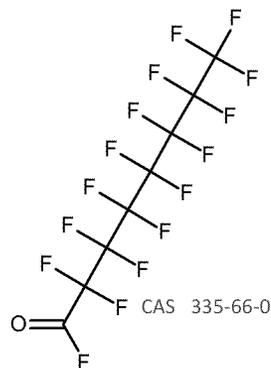
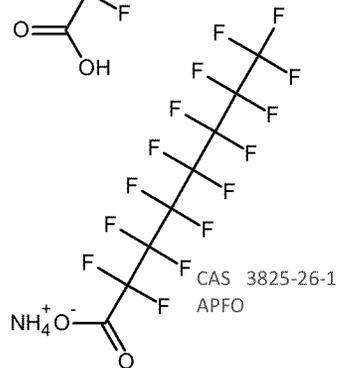
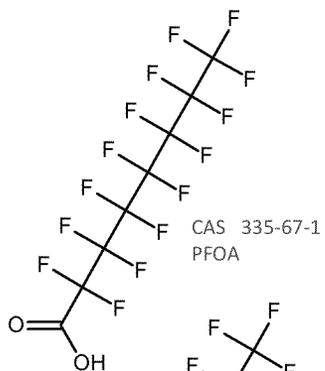
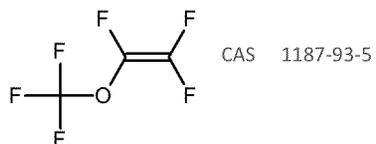
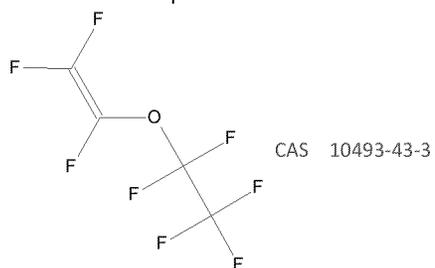
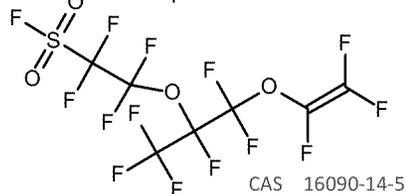
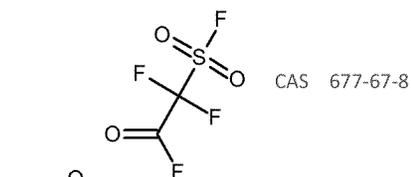
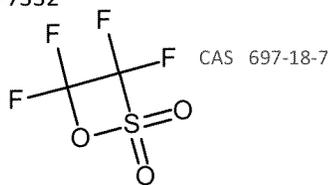


## Current Efforts: EPA/NERL/EMMD

- Completed method validation of PFAS (EPA 24 analyte list) in surface water, waste water and DI water
- Working with NC DEQ and EPA R4 for sample analysis CFR contamination GenX
- Full method validation GenX and 4 other PFECAs in tap water, surface water, waste water (6-26-17)

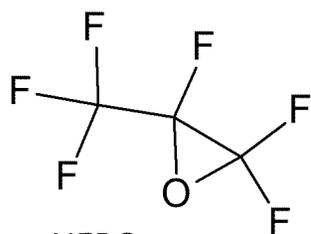
DUPONT FAYETTEVILLE PLANT  
22828 NC HIGHWAY 87 WEST  
FAYETTEVILLE, NC 28306-7332

[http://iaspub.epa.gov/enviro/tsca.get\\_chem\\_info?v\\_registry\\_id=110000559609](http://iaspub.epa.gov/enviro/tsca.get_chem_info?v_registry_id=110000559609)



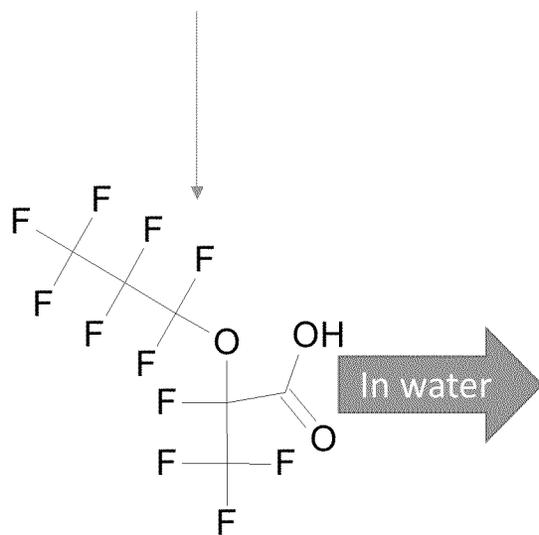
## Hexafluoropropylene oxide (HFPO)

- an intermediate used in industrial organofluorine chemistry
- a monomer for fluoropolymers.
- colourless gas is the epoxide of hexafluoropropylene
- produced by DuPont and 3M and as a precursor to the lubricant Krytox and related materials
- generated by oxidation of perfluoropropylene, e.g. with oxygen as well as other oxidants



HFPO

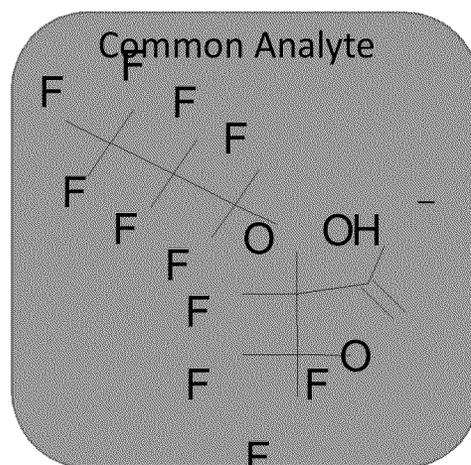
CAS 428-59-1



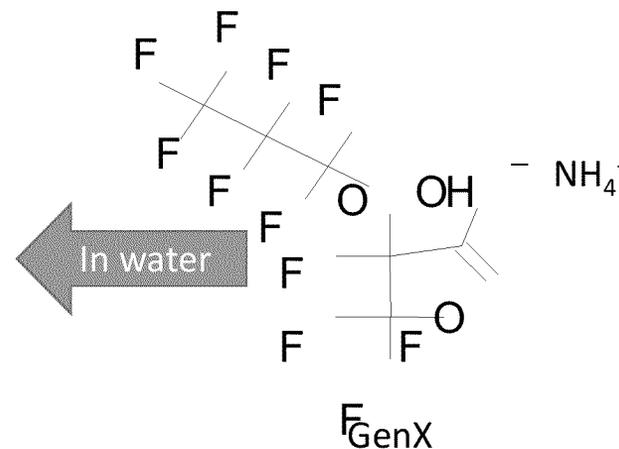
HFPO DA

CAS 13252-13-6

In water



Common Analyte



F-GenX

CAS 62037-80-3

In water

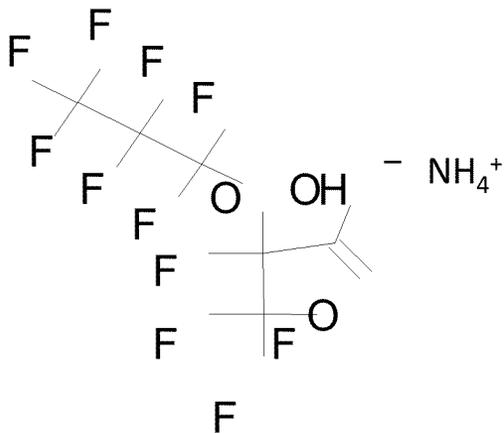
## DuPont™ GenX Processing Aid for Making Fluoropolymer Resins

SETTING A NEW INDUSTRY STANDARD FOR SUSTAINABLE REPLACEMENT TECHNOLOGY

[https://www.chemours.com/Industrial\\_Bakery\\_Solutions/en\\_GB/assets/downloads/Chemours\\_GenX\\_Brochure\\_Final\\_07July2010.pdf](https://www.chemours.com/Industrial_Bakery_Solutions/en_GB/assets/downloads/Chemours_GenX_Brochure_Final_07July2010.pdf)

### GenX Processing Aid

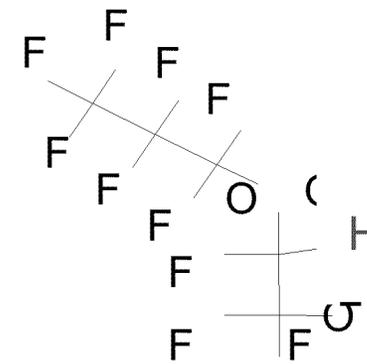
GenX technology includes a new processing aid, which is used only for fluoropolymer resin manufacturing. It has the following chemical structure:  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COOH}\cdot\text{NH}_3$



Likely Air Emission; similar to APFO-PFOA

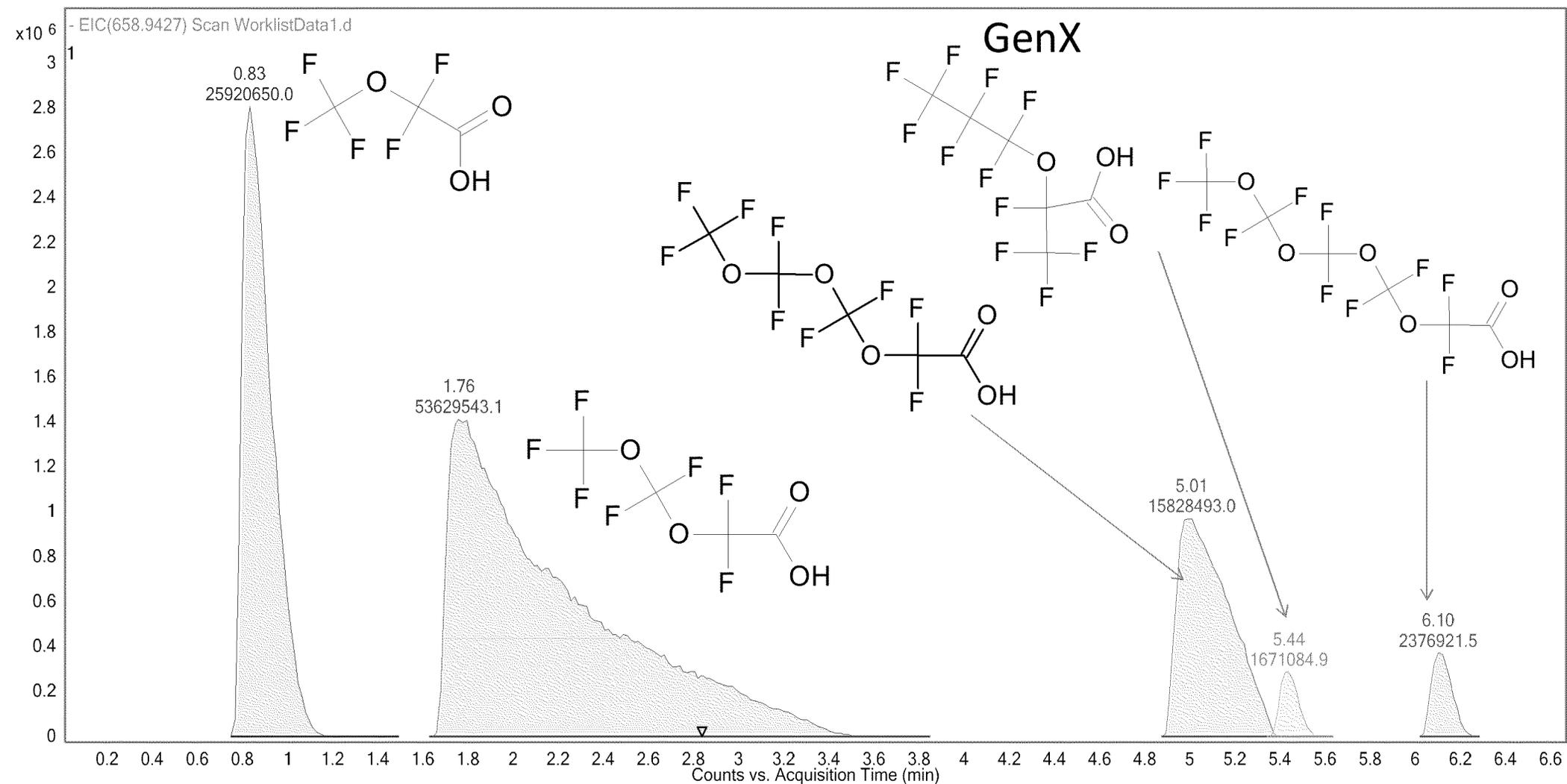
### Thermal Transformation

DuPont resin manufacturing process includes the thermal transformation of the GenX processing aid into a hydrophobic water-insoluble hydride (CAS Number 3330-15-2).



Air Emission?

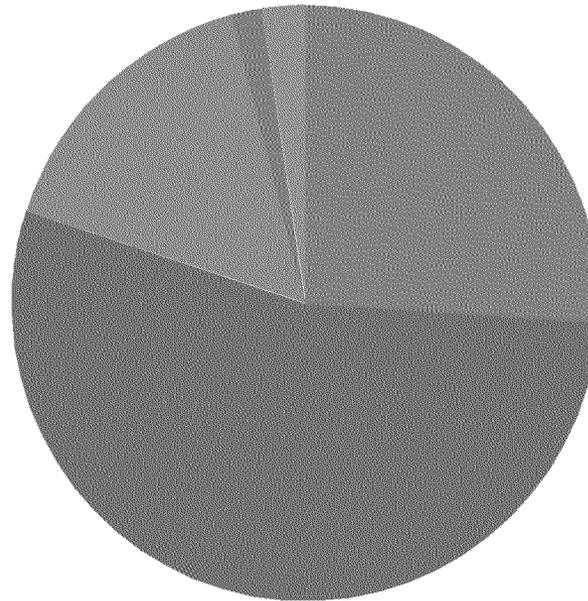
# PFECAs in 5-15-17 Cape Fear River Sample



# PFECAs in 5-15-17 Cape Fear River Sample

Analyte	2[M-H]-	RT	Area	%
C3HF5O3	358.9619	0.83	25,920,650	26.07
C4HF7O4	490.9453	1.76	53,629,543	53.94
C5HF9O5	622.9288	5.01	15,828,493	15.92
GenX	658.9427	5.44	1,671,085	1.681
C6HF11O6	754.9130	6.1	2,376,922	2.391
			99,426,693	100

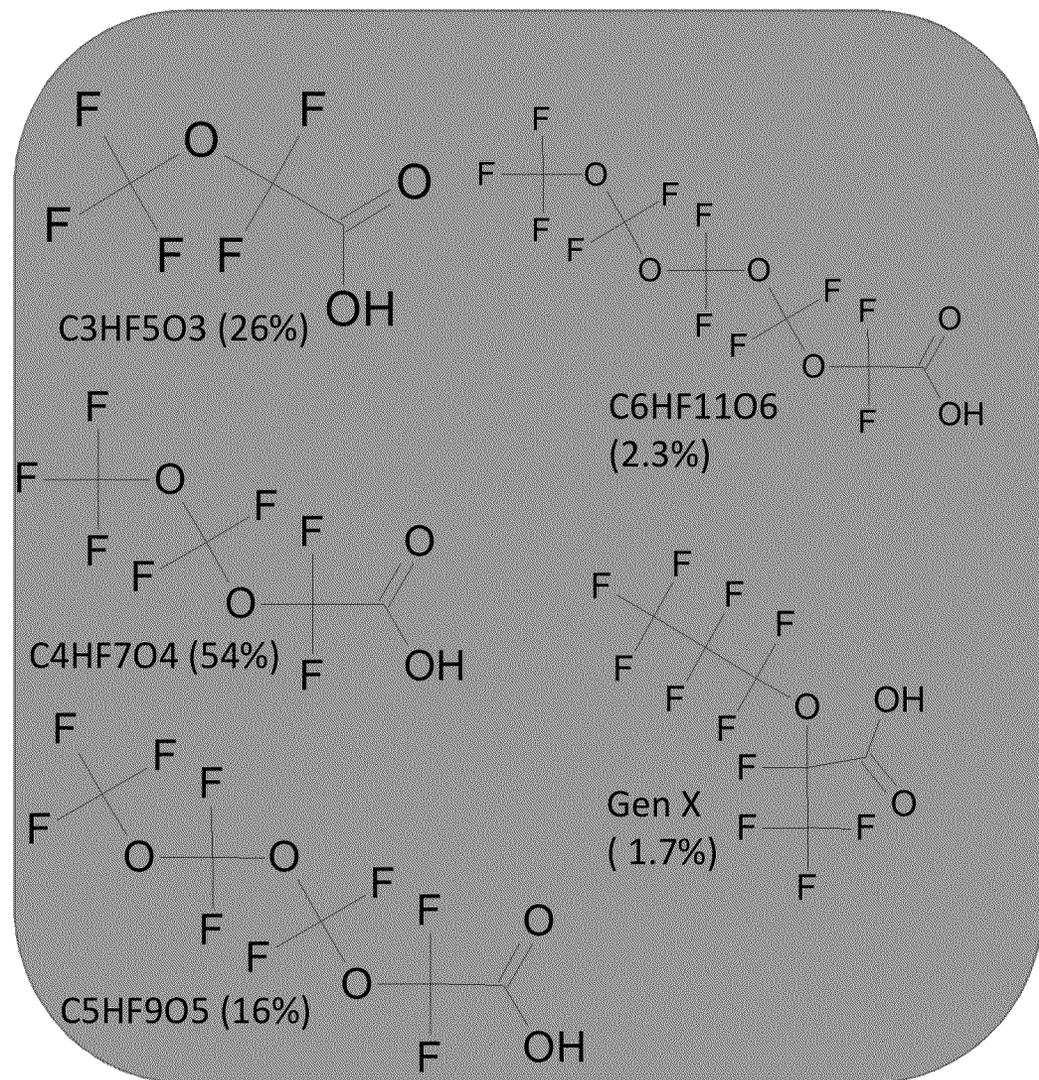
Area



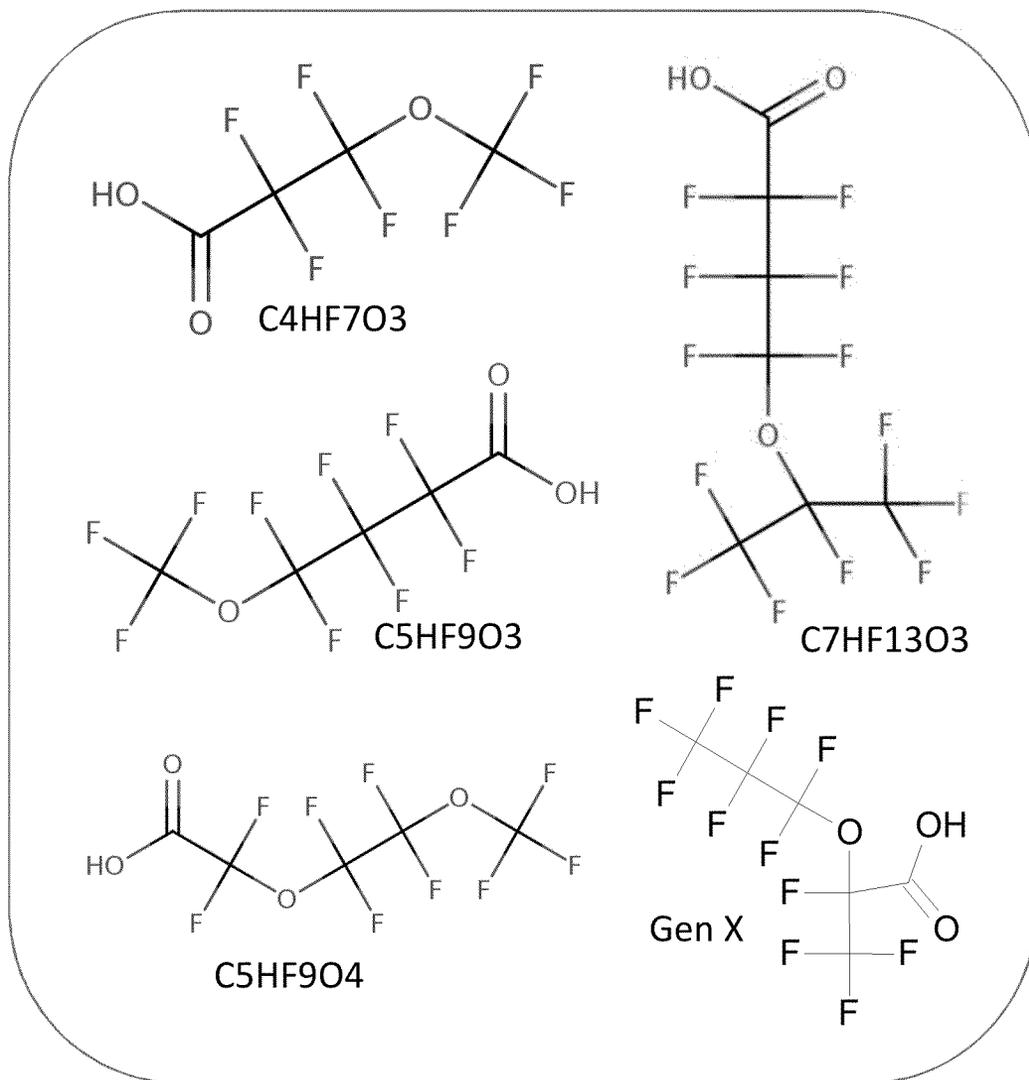
- C3HF5O3
- C4HF7O4
- C5HF9O5
- GenX
- C6HF11O6

And More!

5-15-17 EPA Analysis present in CFR



6-23-17 EPA Quality Assurance Spiked Samples



# PFECAs Method Validation

Figure 1. GenX Method Validation Results. Un-spiked (BL), 50 ng/L (LS) and 200 ng/L (HS) spiked in wastewater, surface water and drinking water.

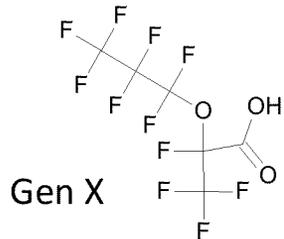
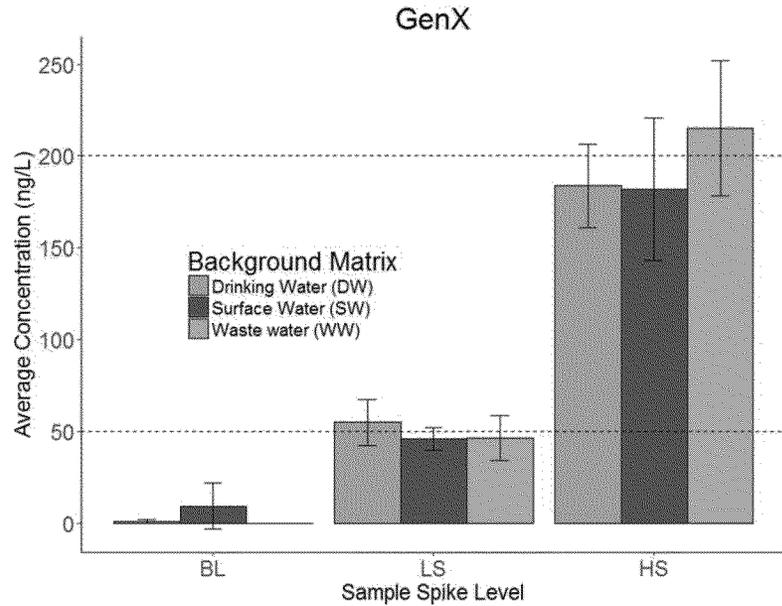
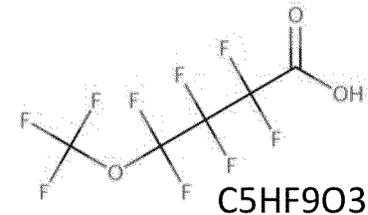
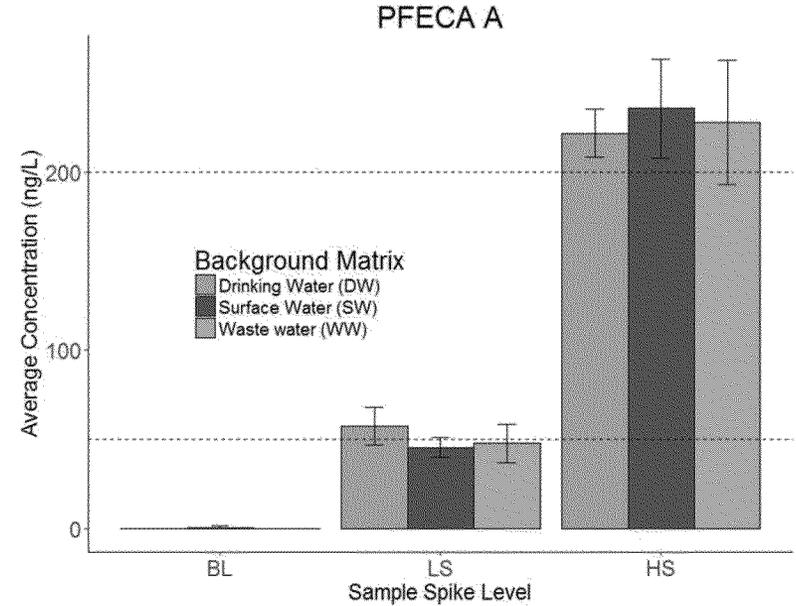


Figure 2. PFECA A Method Validation Results. Un-spiked (BL), 50 ng/L (LS) and 200 ng/L (HS) spiked in wastewater, surface water and drinking water.



# PFECAs Method Validation

Figure 3. PFECA B Method Validation Results. Un-spiked (BL), 50 ng/L (LS) and 200 ng/L (HS) spiked in wastewater, surface water and drinking water.

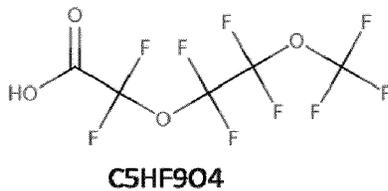
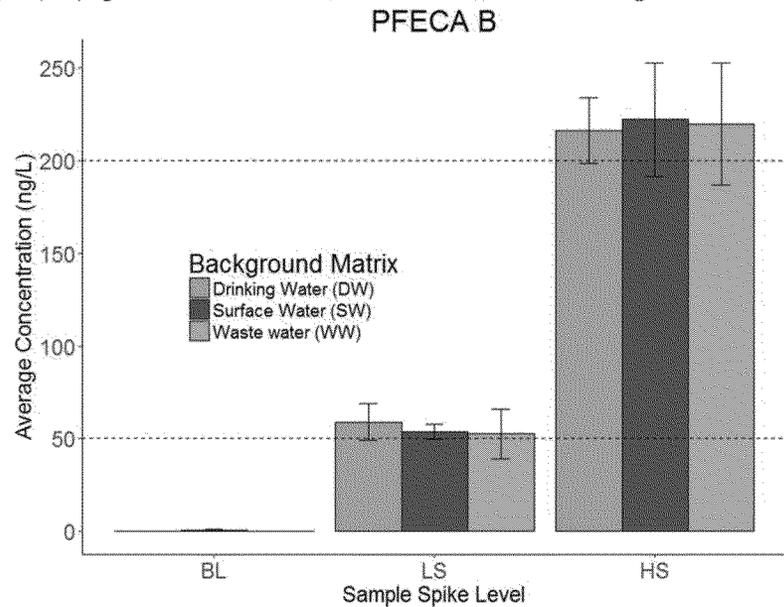
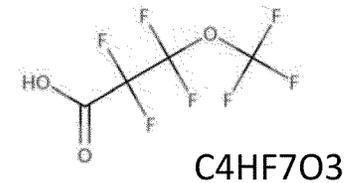
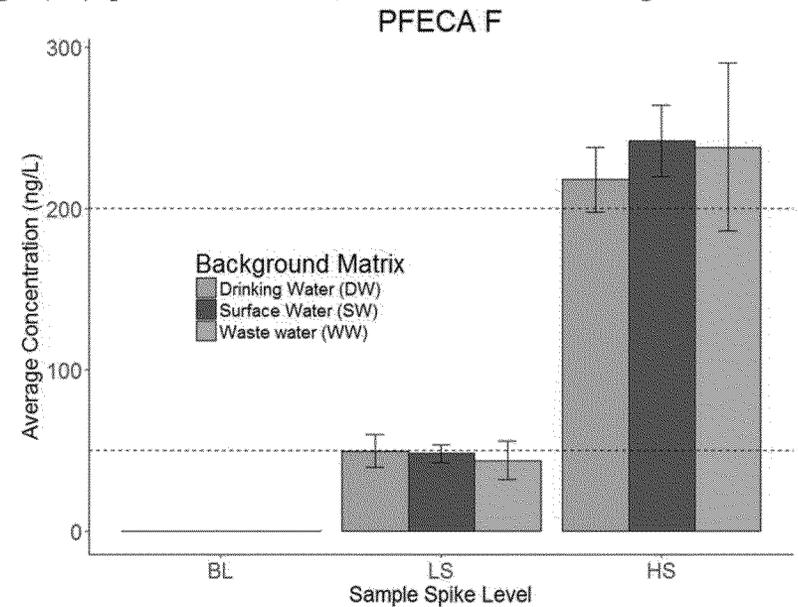


Figure 4. PFECA F Method Validation Results. Un-spiked (BL), 50 ng/L (LS) and 200 ng/L (HS) spiked in wastewater, surface water and drinking water.





[https://www.ncwater.org/basins/Cape\\_Fear/GenXDataspreadsheet.pdf](https://www.ncwater.org/basins/Cape_Fear/GenXDataspreadsheet.pdf)

HFPO-DA (GenX) Analysis June - July 2017													
FRO Location	06/19/2017 results		06/26/2017 results		07/03/2017 results		07/12/2017 results		7/17/2017 results		7/24/2017 results		QA Comments <sup>1,2,3</sup>
	Test America	EPA RTP, NC	Test America	EPA RTP, NC	Test America <sup>4</sup>	EPA RTP, NC	Test America	EPA RTP, NC	Test America	EPA RTP, NC	Test America	EPA RTP, NC	
Hoffer WTP Raw	N/A	N/A	N/A	N/A	13	4	<10						EPA 7/03: Below Limit of Quantitation (LOQ) of 10 ppt TestAmerica 7/03: SURR REC 24%, IS Low TestAmerica 7/12: SURR REC 25%, IS Low
													TestAmerica 6/19: 50X dilution, DUPs 41000 and 36000 [13% RPD], SURR RECs 45 and 48%, MS DNR, IS Low for DUP and MS EPA 6/19: 20X dilution TestAmerica 6/26: 50X dilution, DUPs 18000 and 21000 [15.4% RPD], MS DNR EPA 6/26: 20X dilution EPA 7/03: 20X dilution TestAmerica 7/03: 50X dilution, DUPs 31000 and 28000 [10.2% RPD], MS DNR, IS Low TestAmerica 7/12: 10X dilution
Chemours outfall 002	39000	21760	19000	15250	30000	21530	3300						
													EPA 6/19: 5X dilution TestAmerica 6/26: SURR REC 33%, IS Low TestAmerica 7/03: SURR REC 22%, IS Low TestAmerica 7/12: SURR REC 24%, IS Low
Bladen Bluffs Raw	570	501	36	31	240	168	310						
Bladen Bluffs Raw Duplicate	590		33										
Bladen Bluffs Finished	790		76		190		95						TestAmerica 6/19: 2X dilution, SURR REC 14%, IS Low TestAmerica 7/03: SURR REC 34%, IS Low TestAmerica 7/12: SURR REC 36%, IS Low
Smithfield Foods Well Field	<10		<10		<10		<10						TestAmerica 6/19: SURR REC 9%, IS Low

[https://www.ncwater.org/basins/Cape\\_Fear/GenXDataspreadsheet.pdf](https://www.ncwater.org/basins/Cape_Fear/GenXDataspreadsheet.pdf)

WIRO Location	06/22/2017 results		06/29/2017 results		07/06/2017 results		7/13/2017 results		7/20/2017		7/27/2107		QA Comments <sup>1,2,3</sup>
	Test America	EPA RTP, NC	Test America	EPA RTP, NC	Test America	EPA RTP, NC	Test America	EPA RTP, NC	Test America	EPA RTP, NC	Test America	EPA RTP, NC	
International Paper Raw	810	703	73	41	160	158	110						TestAmerica 6/22: DUPs 810 and 810 [0%RPD], MS 101% EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 20%, IS Low TestAmerica 7/06: SURR REC 35%, IS Low TestAmerica 7/13: SURR REC 23%, IS Low
International Paper Raw DUP						162							
International Paper Finished	690	523	140	111	110	80	31						TestAmerica 6/22: SURR REC 45%, IS Low EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 19%, IS Low TestAmerica 7/06: SURR REC 48%, IS Low
NW Brunswick WTP Finished	910	695	51	52	150	125	110						EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 24%, IS Low TestAmerica 7/13: SURR REC 36%, IS Low
Pender Co. 421 WTP Finished	340	269	160	112	81	68	100						TestAmerica 6/22: SURR REC 8%, IS Low EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 43%, IS Low TestAmerica 7/13: SURR REC 41%, IS Low
LCFWSA Raw	830	629	67	72	150	119	130						TestAmerica 6/22: IS Low EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 24%, IS Low TestAmerica 7/06: SURR REC 33%, IS Low TestAmerica 7/13: SURR REC 24%, IS Low; MS SURR REC 18%, IS Low
CFPUA Sweeney Finished	1100	726	110	100	97	87	110						EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 40%, IS Low TestAmerica 7/13: SURR REC 45%, IS Low
CFPUA – ASR Well	820	588	400	336	190	148	120						EPA 6/22: 5X dilution TestAmerica 6/29: SURR REC 25 %, MS 118% REC, IS Low EPA 6/29: 2X dilution TestAmerica 7/13: SURR REC 42%, IS Low
Wrightsville Beach Well No. 11	26	27	24	28	28	24	29						TestAmerica 6/22: DUPs 26 and 25 [3.9% RPD] TestAmerica 6/29: SURR REC 34%, IS Low TestAmerica 7/06: MS 109% REC